# Synthesis of *nido*- and *closo*-Diplatinacarborane Complexes by Direct Insertion; Crystal and Molecular Structures of *closo*-2,3-$[(Et_3P)_2]_2$-1,2,3,6-$CPt_2CB_5H_7$, *nido*-$\mu$(4,8)-$[(Me_3P)_2Pt]$-8,8-$[(Me_3P)_2]$-7,8,10-$CPtCB_8H_{10}$ and *nido*-8,8-$[(Me_3P)_2]$-7,8,10-$CPtCB_8H_{10}$.

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*Summary* Reaction of *closo*-2,4-$C_2B_5H_7$ with [Pt(styrene)-$(PEt_3)_2$] affords *closo*-2,3-$[(Et_3P)_2]_2$-1,2,3,6-$CPt_2CB_5H_7$, whereas $[Pt(1,5\text{-}C_8H_{12})(PMe_3)_2]$ and 1,6-$C_2B_8H_{10}$ gives *nido*-$\mu$(4,8)-$[(Me_3P)_2Pt]$-8,8-$[(Me_3P)_2]$-7,8,10-$CPtCB_8H_{10}$ which on treatment with activated charcoal affords, *nido*-8,8-$[(Me_3P)_2]$-7,8,10-$CPtCB_8H_{10}$; the structural identity of the complexes was established by *X*-ray crystallography.

DIRECT insertion of $d^{10}$ Ni, Pd and Pt species into 8-, 9- and 11-atom *closo*-carboranes has provided a new approach to the synthesis of both *closo*- and *nido*-metallacarboranes.[1] We now report analogous reactions with 7- and 10-atom carboranes which give hitherto unknown types of bimetallic species.

Treatment (room temperature, 1 h, $Et_2O$) of *closo*-2,4-$C_2B_5H_7$ with $[Pt(styrene)(PEt_3)_2]$ afforded red crystals of (I) (35% yield, m.p. 170 °C decomp.). A single crystal *X*-ray diffraction study established the molecular structure shown (Figure 1). *Crystal data*: $C_{26}H_{67}Pt_2P_4B_5$, $M = 980{\cdot}5$, monoclinic, space group $P2_1$ or $P2_1/m$, $a = 10{\cdot}018(5)$, $b = 18{\cdot}54(1)$, $c = 12{\cdot}648(5)$ Å, $\beta = 126{\cdot}54(5)°$, $U = 1887(2)$ Å$^3$, $D_c = 1{\cdot}724$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 80{\cdot}1$ cm$^{-1}$.

The geometry of the $Pt_2C_2B_5$ cage is that of a highly distorted, tricapped [2 carbons and B(8)] trigonal prism. Although the Pt(2)–Pt(3) separation [3·051(4) Å] represents a relatively weak interaction, the molecule nevertheless constitutes the first proven example of a closed 9-atom

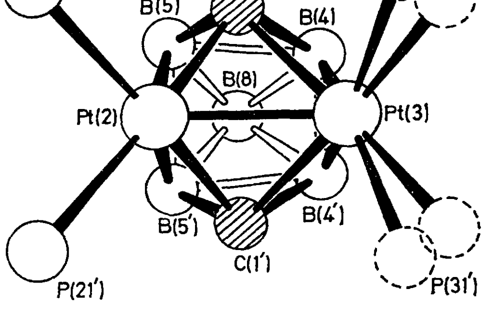

FIGURE 1. Molecular structure of *closo*-2,3-$[(Et_3P)_2]_2$-1,2,3,6-$CPt_2CB_5H_7$. Phosphinoethyl groups are omitted for clarity.

carborane cage incorporating two metal atoms. Space group ambiguity arises since the molecule exhibits local $C_{2v}$ symmetry with one molecular mirror co-planar with the crystallographic *ac* plane. Refinement in the centric space group, however, requires considerable disordering of the phosphine ligands. *R* for this model is currently 0·10 for 2172 reflections (Syntex $P2_1$ diffractometer).

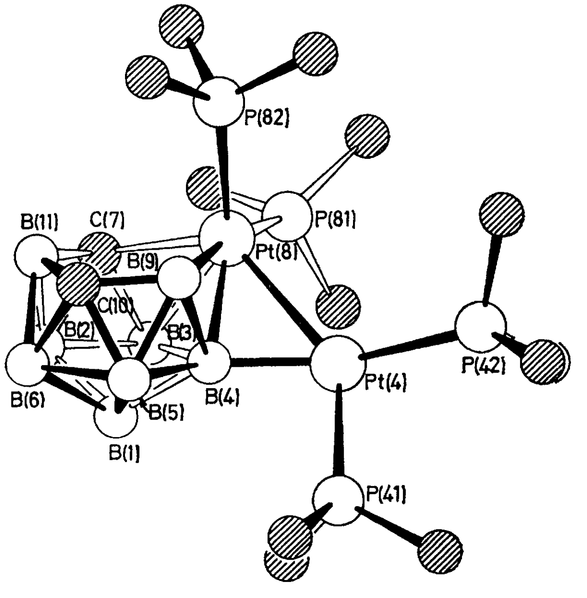

Figure 2. Molecular structure of *nido*-$\mu$(4,8)-$[(Me_3P)_2Pt]$-8,8-$(Me_3P)_2$-7,8,10-$CPtCB_8H_{10}$.

Formation of (I) contrasts with the report[2] that the reaction (room temperature, tetrahydrofuran) of $[Ni(C_2H_4)(PPh_3)_2]$ with *closo*-2,4-$C_2B_5H_7$ yielded initially a violet species, which on chromatography transformed into a $[Ni(C_2B_4H_6)(Ph_3P)_2]$ isomer.†

Treatment (room temperature, petroleum ether) of *closo*-1,6-$C_2B_8H_{10}$ with $[Pt(PMe_3)_2(1,5\text{-}C_8H_{12})]$ gave a yellow crystalline complex (II) [78% yield, m.p. 156 °C decomp.]. A single crystal *X*-ray diffraction study established the structure shown in Figure 2. *Crystal data*: $C_{14}H_{46}Pt_2P_4B_8$, $M = 851{\cdot}02$, monoclinic $A2/a$, $a = 29{\cdot}143(16)$, $b = 10{\cdot}058(7)$, $c = 21{\cdot}935(7)$ Å, $\beta = 90{\cdot}54(4)°$, $U = 6429(6)$ Å$^3$, $D_c = 1{\cdot}758$, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 93{\cdot}5$ cm$^{-1}$, *R* is currently 0·076 for 3153 reflections.

When a solution of (II) in methylene chloride was passed through a column of activated charcoal a $Pt(PMe_3)_2$ unit was displaced, giving the pale yellow crystalline complex (III)‡ [55% yield, m.p. 283 °C]. A crystal structure determination established the molecular geometry shown in Figure 3. *Crystal data*: $C_8H_{28}PtP_2B_8$, $M = 467{\cdot}83$, triclinic, $P\bar{1}$, $a = 9{\cdot}551(3)$, $b = 12{\cdot}321(4)$, $c = 10{\cdot}156(2)$ Å, $\alpha = 107{\cdot}37(2)$, $\beta = 123{\cdot}29(2)$, $\gamma = 91{\cdot}87(2)°$, $U = 924(1)$ Å$^3$, $D_c = 1{\cdot}680$, $Z = 2$, $\mu(\text{Mo-}K_\alpha) = 81{\cdot}3$ cm$^{-1}$, *R* is currently 0·08 for 3428 reflections.

For the mono-platinum species (III), the cage geometry approximates to that of an octadecahedron (11-atom, *closo*-polyhedron) in which Pt(8) occupies the 6- and B(9) and C(7) the 4-connectivity sites. Since, however, the formal interactions Pt(8)–C(10) and Pt(8)–B(11) are non-bonding at 3·10(4) and 2·82(4) Å respectively, the effective connectivity numbers of Pt(8), C(10) and B(11) are four, and the polyhedron possesses an open $\overline{\text{C(7)Pt(8)B(9)C(10)B(11)}}$ face.

The cage of the di-platinum compound (II) is more closely related to a *nido*-icosahedral geometry, having a substantially flatter open face. The second metal atom, Pt(4) lies outside the polyhedral framework and is involved in a 3-centre interaction with B(4) and Pt(8), interatomic separations being Pt(4)–Pt(8), 2·820(2); and Pt(4)–B(4), 2·08(3) Å.

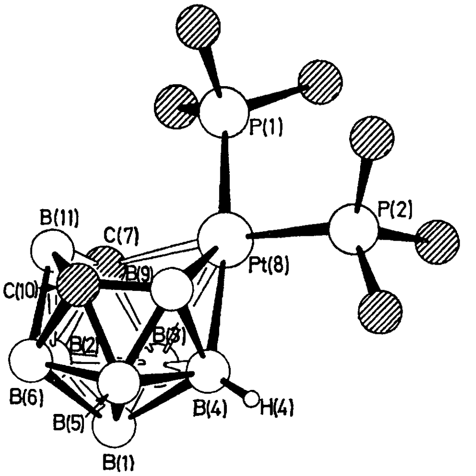

Figure 3. Molecular structure of *nido*-8,8-$[(Me_3P)_2]$-7,8,10-$CPtCB_8H_{10}$.

The $^1H$ n.m.r. spectrum of (II) exhibited signals due to four inequivalent trimethylphosphine ligands. These appeared as doublets with $^{195}Pt$ satellites. One set of doublets showed a further doublet coupling of *ca.* 0·5 Hz. It is thought that this coupling arises from the hydrogen which eventually becomes bonded to B(4) in (III). However, although decoupling experiments indicated that this coupling did not arise from $^{31}P$ or $^{195}Pt$ nuclei, it has not been possible to establish its origin unequivocally. At the present stage of refinement of the crystal structure of (II) it is not possible to make specific comment as to the position of this hydrogen, which could be bonded to an edge- or open face-site.

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† Reaction (vapour phase thermolysis) of *closo*-2,4-$C_2B_5H_7$ with the $\eta^8$ systems $[Fe(CO)_5]$ and $[Co(CO)_2(\eta^5\text{-}C_5H_5)]$ gives,[2,3] respectively, $[(OC)_3FeC_2B_4H_6]$, $[(OC)_3FeC_2B_5H_7]$ and $[(\eta\text{-}C_5H_5)CoC_2B_4H_6]$, $[(\eta\text{-}C_5H_5)CoC_2B_5H_7]$, $[(\eta\text{-}C_5H_5)_2Co_2C_2B_5H_7]$ and $[(\eta\text{-}C_5H_5)_3Co_3C_2B_5H_7]$; the structures of these complexes have so far not been confirmed by *X*-ray crystallography, however, n.m.r. studies show that the $Co_2$ species is not isostructural with (I).

‡ The $^{11}B$ n.m.r. spectrum (32 MHz, $^1H$ decoupled, $CDCl_3$) showed only four resonances of equal intensity at −8·5, 10·3, 12·7 and 26·8 p.p.m. (rel. ext. $BF_3OEt_2$) suggesting that in solution (III) is a dynamic system.

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